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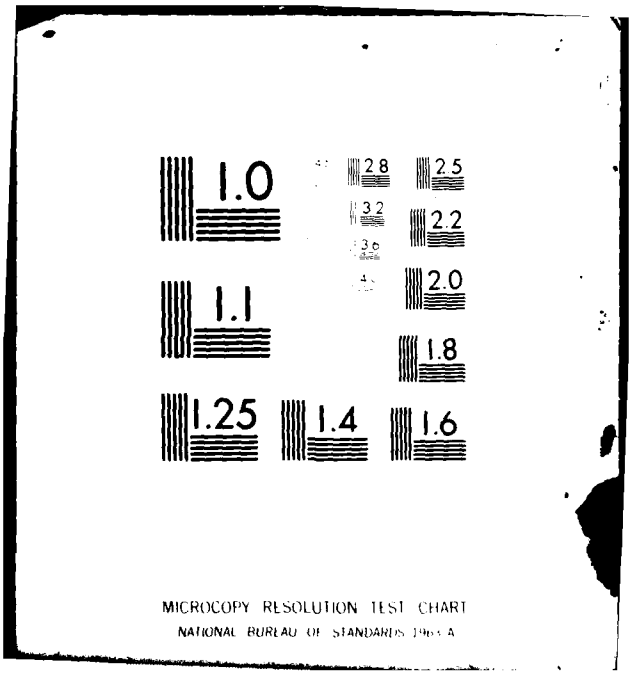
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This program represents part of a continuing study, in progress since 1976, of the elementary processes important in combustion, flame and ignition phenomena. In the course of pursuing this research we have developed significantly new experimental techniques for studying atom and radical reactions and new theoretical models for those processes. We have, in addition, extended our efforts to include ionic processes and the effects of solvents on both radical and ionic reactions.



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FINAL REPORT ON THE PROJECT

# "INVESTIGATION OF GAS PHASE REACTIONS OF IMPORTANCE IN IGNITION PROCESSES"

Sidney W. Benson
Professor of Chemistry

29 January 1982

U. S. ARMY RESEARCH OFFICE

Grant No. DAAG-29-76-G-0195—USC 53-4815-1640

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## GOALS

This program represents part of a continuing study, in progress since 1976, of the elementary processes important in combustion, flame and ignition phenomena. In the course of pursuing this research we have developed significantly new experimental techniques for studying atom and radical reactions and new theoretical models for those processes. We have in addition extended our efforts to include ionic processes and the effects of solvents on both radical and ionic reactions.

## Summary of Important Results

1. Perhaps our most important result is the construction for the first time of a comprehensive molecular mechanism which is capable of representing quantitatively the oxidation of hydrcarbons at low and at high temperatures, in liquid state and in gases [350]. It describes as well, induction periods, periodic cool flames and the transition to hot ignition. Interestingly it can also describe atmospheric oxidation (air pollution).

2. Our next most important or perhaps equally important result has been the development of the technique of the "Very Low Pressure Reactor" (VLPR). With this we have been able to measure heats of formation of free radicals to about ±0.1 kcal. This represents an order of magnitude improvement over current techniques. The same apparatus also permits making kinetic measurements on radical reactions with better accuracy than any of the current flow techniques [327,331,351,355].

3. We have completed studies on a number of key radicals, obtaining values for their heats of formation and entropies. They are $CH_3$, t-butyl, cyclopropyl, $HO_2^{\cdot}$, $RO_2^{\cdot}$ (R=alkyl, acyl); $HO_n^{\cdot}$ (n=3,4,5); $RO_n^{\cdot}$ (n=2,3,4,5); $HS^{\cdot}$; $MeS^{\cdot}$ and a number of chlorinated radicals, $\dot{C}HCl_2$; $\dot{C}H_2Cl$; $C_2Cl_5$, and $C_2HCl_3$ [327,329,330,331,332,336,337,338,342,343,344,351,353].

4. We have directed attention to the importance of metals in the chemistry of the stratosphere and their potential for influencing the halogen concentrations and the ozone levels [349].

5. Another very important development which is still in progress is the development of a theoretical, molecular model capable of describing

the structure and thermochemistry of solvated ions. Currently we can reproduce the gas phase data on aquation of alkali cations $M(H_2O)_n^+$ ($n = 1,\cdots,6$) and halide cations $X(H_2O)_n^-$ [papers in press].

6. An analysis of well-stirred reactors has been made which permits independent observation of initiation rates, propagation rates and termination rates in fast flow systems [356].

7. We have shown that a number of, what have been interpreted as metathesis reactions are really complex reactions initiated by radical recombination and subsequent fission via a different channel. A general theory of radical-radical reactions is now under development [354].

8. We have elucidated the elementary channels involved in ozone chemistry at low temperatures including ionic pathways and generated rate parameters for all steps [340].

LIST OF PERSONNEL

a. Sidney W. Benson, Principal Investigator (Professor of Chemistry)
b. Morton Richelson, (Post-doctorate, 1/8 time) — 1 year
c. Peter A. Knoot (Post-doctorate, 1/2 time) — 1 year
d. Palle Pagsberg (Research Scientist 1/2 time) — 1 year
e. Lilian Shum (Graduate Student 1/2 time) — 2 years
f. Roger Lewis (Post-doctorate 1/2 time) — 1 year
g. Shawn Heneghan (Graduate Student, 1/4 time) —2 years
h. Maia Vaisman (Graduate Students, 1/4 time) — 1 year
i. Peter Hadju (Post-doctorate, 1/2 time) — 1 year
j. Thimme Gowda (Post-doctorate, 1/4 time) — 1 year
k. Prakash S. Nangia (Post-doctorate, 1/2 time) — 2 years
l. Emil Ratajczak (Post-doctorate, 1/2 time) — 1 year

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